## REACTION OF DIAZOMETHANE WITH p-QUINOLIDE COMPOUNDS

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As a continuation of our research [1,2] on the reaction of diazoalkanes with various types of quinoid compounds, in the present paper we studied the reaction of diazomethane (DAM) with p-quinolide compounds. Previously it was mentioned [3] that o-quinolide compounds add DAM at the multiple bonds of the carbon ring. We used the following p-quinolide derivatives as the starting compounds.



It proved that the bromoquinolide compounds react with DAM with exceeding ease, with the intense liberation of nitrogen and the formation of the products of inserting the  $CH_2$  group in the C-Br bond by the following probable mechanism:



An alternate reaction mechanism can be the insertion of the methylene, formed by the decomposition of DAM, at the C-Br bond, which seems less probable, since the reaction was run in the dark and at low temperatures.

For both of the quinobromides  $(R' = CH_3, R'' = Br \text{ and } R' = C(CH_3)_3, R'' = Br)$  the addition products of DAM to the quinoid ring could not be detected. However, besides the quinolide derivative (II), spiran (IV) is formed when DAM is reacted with 4-bromo-4-methyl-2,6-di-tert-butyl-2,5-cyclohexadien-1-one. The formation of (IV) can be associated both with the spontaneous isomerization of the starting quinobromide to benzyl bromide (III) and reaction of the latter with DAM, and with the reaction of DAM with the quinomethide that is formed by the cleavage of HBr from the starting quinobromide [4].

We studied the reaction of DAM with benzyl bromide (III) under analogous conditions. The reaction proceeds ambiguously and leads to the formation of spiran (IV) in 28% yield and small amounts of the substituted bromoethane (V) and stillbene quinone (VI).

Bromoethane (V) and stilbene quinone (VI) were not detected in the reaction products of DAM with quinobromide (I). Consequently, the appearance of spiran (IV) in the reaction mixture is evidently associated more with the intermediate formation of the quinomethide than with the spontaneous isomerization of the starting quinobromide (I) to benzyl bromide (III).

In contrast to the quinobromides, the 4,4-dialkyl-2,6- tert-butyl-2,5-cyclohexadienones do not react with DAM, despite an increase in the reaction time, the temperature, and the DAM concentration. The 4-morpholyl

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and 4-methoxy-2,4,6-tri-tert-butyl-2,5-cyclohexadien-1-ones, 1,3,5-tri-tert-butyl-2,5-cyclohexadien-4one peroxide, and spiran (IV) also proved to be inert toward DAM. In all of the indicated cases the starting p-quinolide compounds were recovered quantitatively.

## EXPERIMENTAL

The UV spectra were obtained on an SF-4 instrument in hexane solution. The IR spectra were taken on a Hitachi EPI-510 spectrometer (as KBr pellets). The NMR spectra were obtained on a Varian HA-100 instrument in  $CCl_4$  solution at 25°C.

<u>4-Bromomethyl-2,4,6-tri-tert-butyl-2,5-cyclohexadien-1-one (II)</u>. To a solution of 1.7 g (0.005 mole) of 4-bromo-2,4,6-tri-tert-butyl-2,5-cyclohexadien-1-one (I)  $[R' = C(CH_3)_3]$  in 20 ml of ether was added 25 ml of an ether solution of DAM [from 2.06 g (0.02 mole) of nitrosomethylurea]. The mixture was kept in the dark for 2 days. The ether was distilled off. Separation from the starting product and tars was effected by TLC on Silufol UV-254 plates, using a hexane-benzene system (2:1 volume ratio) for elution. The yield of (II)  $[R' = C(CH_3)_3]$  was 0.58 g (32.8%), mp 109-110° (from hexane). Ultraviolet spectrum:  $\lambda_{max}$  240 nm (log  $\epsilon$  4.023). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1650, 1670 (CO). NMR spectrum ( $\delta$ , ppm): 0.96 [p-C(CH\_3)\_3]; 1.20 [o-C-(CH\_3)\_3]; 3.58 (CH\_2); 6.28 (H<sub>m</sub>). Found: C 64.41; H 8.74%. C<sub>19</sub>H<sub>31</sub>OBr. Calculated: C 64.22; H 8.79%.

4-Bromomethyl-4-methyl-2, 6-di-tert-butyl-2, 5-cyclohexadien-1-one (Π) and 4, 6-Di-tert-butylspiro-[5.2]-3, 6-octadien-5-one (IV). To 1.5 g (0.005 mole) of 4-bromo-4-methyl-2, 6-di-tert-butyl-2, 5-cyclohexadien-1-one (I) (R' = CH<sub>3</sub>) in 20 ml of ether was added 25 ml of an ethereal solution of DAM. The mixture was kept for 2 days. The ether was distilled off. A chromatographic column was used for the separation, using silica gel L, 100/160  $\mu$ , as the support and a hexane-benzene system, volume ratio 2:1, for elution. The yield of (Π) (R' = CH<sub>3</sub>) was 0.65 g (41.4%), mp 59-60° (from hexane). Ultraviolet spectrum:  $\lambda_{\text{MEX}}$  236.5 nm (log ε 3.924). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>); 1635, 1665 (CO). NMR spectrum ( $\delta$ , ppm): 1.19 [C(CH<sub>3</sub>)<sub>3</sub>]; 1.29 (CH<sub>3</sub>); 3.30 (CH<sub>2</sub>); 6.38 (H<sub>m</sub>). Found: C 61.17; H 8.19%. C<sub>16</sub>H<sub>25</sub>OBr. Calculated: C 61.34; H 8.04%. The yield of (IV) was 0.38 g (32.6%), mp 105-106° (from hexane); cf. [5].

<u>4,6-Di-tert-butylspiro[5.2]-3,6-octadien-5-one (IV)</u>. To 1.5 g (0.005 mole) of 3,5-di-tert-butyl-4hydroxybenzyl bromide (III) in 20 ml of ether was added 25 ml of an ether solution of DAM. The mixture was kept at  $\sim 20^{\circ}$  for 2 days. The ether was distilled off. The separation was done on a chromatographic column under the above-described conditions. The yield of (I) was 0.35 g (28.6%).

## CONCLUSIONS

The reaction of diazomethane with bromoquinolide compounds leads to the insertion products of the  $CH_2$  group at the C-Br bond, whereas other p-quinolide compounds proved to be inert in this reaction.

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